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Novel highly active and selective Cu-Ni based methanol synthesis catalyst

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Introduction

Methanol is an efficient fuel in an internal combustion engine or in a fuel cell, and it has therefore been suggested as an alternative energy carrier [1]. Despite the significant methanol production nowadays, the replacement of gasoline would however require more than a hundredfold increase in methanol production [2]. Moreover, deactivation of the commercial Cu/ZnO methanol synthesis catalyst poses one of the biggest problems. More than one third of the activity is lost after the first 1000 h of operation, something that often determines the economic lifetime of the catalyst [3]. It would therefore be of great value, if methanol synthesis catalysts with greater activity and stability could be developed. Based on a screening of a large number of bimetallic alloys using a newly developed microkinetic model, we have constructed volcano plots for methanol synthesis. The theoretical turnover frequency (TOF) is plotted as a function of two descriptors, namely the carbon and oxygen binding energies and Cu/Ni alloys are suggested as active methanol synthesis catalysts [4]. Herein, we present catalytic test results, characterization and extensive density functional theory (DFT) calculations for the CO hydrogenation over Cu/Ni bimetallic alloys [5].

Experimental

Cu/Ni based catalysts were prepared by the incipient wetness impregnation method. The catalyst precursors were dried at 100 °C and directly reduced in the reactor with 1% H₂ in N₂ flow at 280°C for 12 h. Performances of catalysts for high-pressure CO hydrogenation have been evaluated in a fixed-bed, continuous-flow reactor with a GC-FID/TCD detection system [6]. Typical reaction conditions were: P=100 bar; T=250-300°C. Reduction processes and phase compositions were investigated using in-situ XRD. The activity based on the amount of active materials was compared to a Cu/ZnO/Al₂O₃ model catalyst similar to the systems used in industry. Additionally, *in-situ* X-ray diffraction (XRD), *in-situ* X-ray adsorption spectroscopy (XAS) and *in-situ* transmission electron microscopy (TEM) have been used to clarify the structure of the Cu/Ni catalysts.

Results and Discussion

Figure 1 shows the theoretical activity volcano for the production of methanol from CO and H₂. Cu is observed to be closest to the top of the volcano among the transition metals, and there are several bimetallic alloys within the same region. An interesting alloy found in the screening procedure is Cu₃Ni. Figure 1 shows that one of the possible step sites of this alloy, denoted ^{AA}Cu₃Ni, is predicted to possess a

higher methanol synthesis activity than the step site of pure Cu metal. Table 1 shows that the methanol space time yields (STY) for a CuNi/SiO₂ catalyst indeed were at the same level as the STY's for the Cu/ZnO/Al₂O₃ model catalyst.

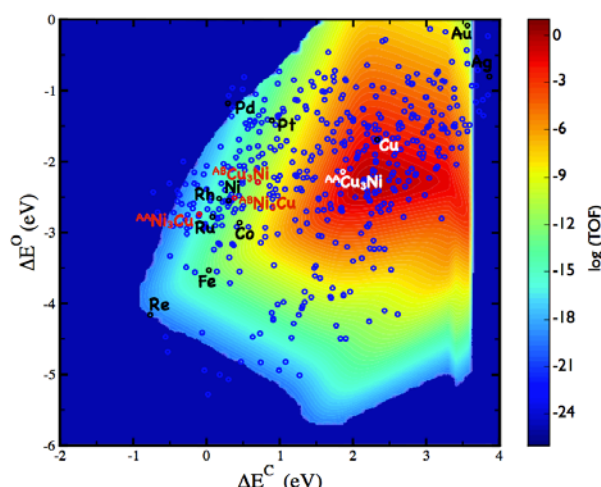


Figure 1. Theoretical activity volcano for the production of methanol from CO and H₂. The turnover frequency is plotted as a function of carbon and oxygen binding energies for a range of binary alloys. Two different steps for either of Cu₃Ni and CuNi₃ alloys are depicted in red; the Cu step of Cu₃Ni is depicted in white. Reaction conditions are 523 K, 45 bar H₂, 45 bar CO, and 10 bar methanol.

Table 1. Behavior of CuNi/SiO₂ and Cu/ZnO/Al₂O₃ catalysts in CO hydrogenation at steady state at 100 bar, and H₂/CO = 1.0 vol/vol.

Catalysts	T [°C]	GHSV [h ⁻¹]	CO conv. [mol%]	Carbon based, CO ₂ -free selectivity [mol%]			MeOH _{STY} ^{b)} g/(g _{active materials} ·h)
				MeOH	C ₂ + oxygenates	HC ^{a)}	
CuNi/SiO ₂	275	5200	5.2	98.2	1.4	0.4	1.6
CuNi/SiO ₂	300	5200	8.2	98	1.4	0.6	3.3
Cu/ZnO/Al ₂ O ₃	275	16000	13.5	97.6	2.1	0.3	1.7
Cu/ZnO/Al ₂ O ₃	300	32000	12.7	96.3	2.8	0.9	3.7

^{a)} HC: hydrocarbons. ^{b)} STY: space time yield of methanol based on the amount of active materials (0.175 g metallic Cu + Ni for CuNi/SiO₂ catalyst, 0.71 g Cu + ZnO for Cu/ZnO/Al₂O₃ catalyst according to elemental analysis according to elemental analysis) in 1 g catalyst precursor.

Conclusions

In-situ XRD shows that only the CuNi alloy is present in the reduced catalyst. It seems likely that the surface after reduction is enriched in Cu and that CO can pull Ni out onto the surface. In-situ XAS shows that Cu and Ni can be reduced simultaneously. The high activity of silica supported CuNi alloy catalyst agreed with the fact that the DFT calculations identified Cu rich CuNi alloy catalysts as highly active catalysts for the hydrogenation of CO to form methanol.

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